

## **'Ab Initio' Molecular Dynamics of Hydrated Triflic Acid**

S.J. Paddison, L.R. Pratt, and T.A. Zawodzinski, Jr.

*Los Alamos National Laboratory*

*Los Alamos, NM 87545 USA*

We present results of 'ab initio' molecular dynamics for hydrated triflic (trifluoromethane sulfonic acid,  $\text{CF}_3\text{SO}_3\text{H}$ ) acid obtained with the Vienna Ab Initio Simulation Program (VASP) computational package. Simulation calculations initiated from the known ion-paired  $\text{H}_3\text{O}^+\cdot\text{CF}_3\text{SO}_3^-$  structures of the hydrated crystals for varying water content will be compared with the experimental structures to test the accuracy of current 'ab initio' molecular dynamics computational techniques for these systems. Attention will be specifically directed to the rotational and vibrational dynamics of the hydronium ( $\text{H}_3\text{O}^+$ ) ion present in these crystals. The vibrational density of states will be used to analyze the experimental vibrational spectroscopy of these systems. The vibrational density of states together with the energies obtained, studied as a function of temperature, will be used to estimate absolute free energies of these crystals. These thermodynamic properties will be used to model the water content of polymer electrolyte membranes of Nafion® type as a function of water activity. The dynamics associated with proton transfer between triflic acid and a neighboring water molecule will be studied on the basis of classical trajectories initiated from un-ionized molecular configurations obtained from molecular orbital calculations of the isolated cluster  $\text{H}_2\text{O}\cdot\text{CF}_3\text{SO}_3\text{H}$ .